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# Thermodynamic Properties of $M_2EO_4$ , $M_2Mo_xO_{3x + 1}$ and Double Chromates (M = Li, Na, K, Rb, Cs; E = Cr, Mo, W)

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**Abstract**—The phase transition temperatures of chromates and molybdates of certain alkali metals, and the melting temperature and enthalpy of polymorphic transformations for tungstates, are determined by means of thermal analysis. Enthalpies of dissolution of rubidium and cesium chromates in water and enthalpies of dissolution of alkali metal tungstates in a melt at 923 K are measured via calorimetry. Standard enthalpies of formation of sought chromates are calculated. The linear correlations between the enthalpies of formation of sulfates, selenates, chromates, tungstates, and molybdates are established, and a linear correlation within

 $(\Delta G_{0x}^{\circ})^{-1} - ((\Delta MV)_{0x})^{-1}$  coordinates is found for isopolymolybdates.

*Keywords:* thermal analysis, dissolution calorimetry and high-temperature microcalorimetry in the melt, chromates, molybdates and tungstates of alkali metals, double chromates and molybdates, phase transition temperatures, linear correlations

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### **INTRODUCTION**

The thermodynamic properties of sought compounds have been studied in numerous works and systematized in [1]. Later publications presented new data for cesium and rubidium isopolymolybdates. For many isopolymolybdates, no thermodynamic characteristics are available. In this work, we therefore continue the study of the polymorphic transitions and melting temperatures of a series of chromates and molybdates via thermal analysis according to a unique approach. Rubidium and cesium chromates and tungstates are also studied by means of calorimetry.

#### EXPERIMENTAL

Molybdates and tungstates were prepared via stepwise solid-phase synthesis from stoichiometric mixtures of the carbonate of the corresponding alkali metal (analytical grade) and molybdenum oxide (special purity grade) or tungsten oxide (special purity grade). Synthesis was conducted at temperatures from 550 K to the temperatures of melting or below the temperatures of melting for incongruently melting salts. The compounds were studied via X-ray phase analysis, and the crystal structure for isopolymolybdates was determined [2]. Potassium, rubidium and cesium chromates (analytical grade) recrystallized from water were dehydrated via calcination to 500–550 K.

The melting and phase transition temperatures of chromates, tungstates, and molybdates, along with

those of isopolymolybdates, were determined via thermal analysis on an OD-102 derivatograph (MOM). Heating thermographs (rate, 8–10 K/min) and cooling thermographs (with the heater switched off) were recorded in cylindrical platinum crucibles. The standard was a  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder prepared from a single crystal. Five to seven parallel experiments were performed for each compound. Thermocycling was used for some compounds (Fig. 1), allowing us to determine the character of their melting and their thermal stability. The absence of peak splitting upon the solidification of a melt and the coincidence of melting and solidification temperatures (within the experimental error) testified to the congruent character of melting.

The enthalpies of polymorphic transitions  $M_2WO_4$ (M = Li, Na, K, Rb, Cs) were determined via thermal analysis using internal standards. The melting enthalpies of sodium tungstates and the enthalpies of the polymorphic transformations of sodium and potassium tungstates, selected from the most reliable literature data and obtained via differential scanning calorimetry (DSC), were used as standards. The areas of peaks corresponding to the effect of melting or polymorphic transformation were determined from the DTA curve via graphic integration.

To determine the enthalpies of formation of rubidium and cesium chromates, the enthalpies of dissolution of these salts were measured in water in a variable temperature liquid calorimeter [3] at 298.15  $\pm$  0.1 K,



Fig. 1. Thermograph of  $Rb_5Pr(CrO_4)_4$ , thermocycling mode

with the formation of solutions having concentrations of 0.0091 and 0.0093 mol/L. The volume of the calorimeter cell was 160 mL. The temperature probe was a KMT-14 thermistor with a thermometric sensitivity of  $1 \times 10^{-4}$  K. The calorimeter was calibrated electrically. Its reliability was verified using the enthalpies of dissolution of KCl and Tris in water. The results from our measurements are given in Table 1.

High-temperature microcalorimetry was used to measure the enthalpies of dissolution of alkali metal tungstates [4, 5]. The enthalpies of dissolution in a melt with the composition  $3Na_2O \cdot 4MoO_3$  were measured at 923 K in a platinum calorimeter cell with a volume of 25 mL. A differential thermobattery of 144 junctions of Pt-Pt/Rh thermocouples served as a measuring sensor. The calorimeter was calibrated using the enthalpy of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (99%) and tested over the dissolution enthalpies of MgO and WO<sub>3</sub> at 923 K in the  $3Na_2O \cdot 4MoO_3$  melt. The results from measuring the enthalpies of dissolution of  $WO_3$ ;  $Cs_2CO_3$ ; and lithium, sodium, potassium, rubidium, and cesium tungstates at 923 K are given in Table 2.

Table 1. Enthalpies of dissolution of rubidium and cesium chromates in water

Composition	C, mol/L	п	$\Delta H^{\circ}_{298,sol},$ kJ/mol
Rb <sub>2</sub> CrO <sub>4</sub>	0.0091	7	$23.3\pm0.3$
Cs <sub>2</sub> CrO <sub>4</sub>	0.0093	8	$27.6\pm0.4$

C is the concentration of the solution, and n is the number of experiments.

## **RESULTS AND DISCUSSION**

Our results from measuring the melting and phase transition temperatures are compared to data from [1] in Table 3.

Temperature interval  $T_{init} - T_{fin}$  is given in Table 3 for the phase transition (melting). The temperature of the onset of the effect  $(T_{init})$  corresponds to the transformation (melting) of the first crystals of the compound in direct contact through the wall of the platinum crucibles with the thermocouple junction. This temperature is therefore preferable as the choice of the phase transition temperature. The final temperature  $(T_{\rm fin})$  corresponds to termination of the effect in the total mass of the sample. The mass be quite high, since this is necessary for a more reliable estimate of the enthalpy of the phase transition. With an appreciable drop in the mass of the sample (as in modern DSC), difference  $T_{\text{init}} - T_{\text{fin}}$  will be minimized. The divergences of the temperatures of transformations in different works could be due to the choice of  $T_{init}$  or  $T_{fin}$ . In earlier works, this could also have affected the quality of synthesis.

The values of the enthalpies of phase transitions, calculated from the heating and cooling curves, are in agreement within 6%, and the deviations of the values obtained in this work from those of the reference data do not exceed 20%. The maximum error of determining the enthalpies of transformations is thus no greater than 20%. The calculated values of the enthalpies of transformations are compared to the reference values from [1] in Table 4.

The data in Table 1 were used to calculate the standard enthalpies of formation of Rb<sub>2</sub>CrO<sub>4</sub>(cr) and  $Cs_2CrO_4(cr)$ . On the basis of the equations for reactions (1) and (2) of the dissolution of salts,

$$Rb_{2}CrO_{4}(cr) + 6000H_{2}O$$
  
=  $2Rb_{(sol,H_{2}O)}^{+} + CrO_{4(sol,H_{2}O)}^{2-},$  (1)

$$Cs_{2}CrO_{4}(cr) + 5870H_{2}O$$
  
=  $2Cs_{(sol H,O)}^{+} + CrO_{4(sol H,O)}^{2-}$  (2)

and using the enthalpies of formation of the ions [1] formed in the solutions, we calculated the standard enthalpies of formation of Rb and Cs chromates:

$$\Delta_{\rm f} H_{298}^{\circ} [\rm Rb_2 CrO_4 (\rm cr)] = -1411.6 \pm 3.1,$$
  
$$\Delta_{\rm f} H_{298}^{\circ} [\rm Cs_2 CrO_4 (\rm cr)] = -1430.0 \pm 3.1 \text{ kJ/mol}.$$

These values are in agreement with those accepted in [1]  $(-1415.6 \pm 3.8 \text{ and } -1434.0 \pm 3.4)$  within the error of our thermochemical experiment. The recommended values as arithmetic means are therefore

$$\Delta_{\rm f} H_{298}^{\circ} [\rm Rb_2 CrO_4(cr)] = -1413 \pm 3.0,$$

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**Table 2.** Enthalpies of dissolution of WO<sub>3</sub>,  $Cs_2CO_3$ , and  $M_2WO_4$  (M = Li, Na, K, Rb, Cs) in a  $3Na_2O \cdot 4MoO_3$  melt

Compo- sition	N	$\Delta H_{923,sol}^{\circ},$ kJ/mol	Compo- sition	N	$\Delta H_{923,sol}^{\circ},$ kJ/mol
Li <sub>2</sub> WO <sub>4</sub>	8	$46.9\pm0.4$	Cs <sub>2</sub> WO <sub>4</sub>	11	$6.7\pm0.3$
Na <sub>2</sub> WO <sub>4</sub>	9	$23.0\pm0.3$	Cs <sub>2</sub> CO <sub>3</sub>	8	$-30.6\pm0.6$
K <sub>2</sub> WO <sub>4</sub>	7	$8.9\pm0.4$	WO <sub>3</sub>	15	$30.7\pm0.2$
Rb <sub>2</sub> WO <sub>4</sub>	9	$6.8\pm0.4$	_	_	—

$$\Delta_{\rm f} H_{298}^{\circ} [\rm Cs_2 CrO_4(cr)] = -1432 \pm 2.9 \, \rm kJ/mol.$$

The enthalpies of dissolution of  $Cs_2WO_4(cr)$  and  $Cs_2CO_3(cr)$  in the melt (Table 3) allow calculations using the thermochemical cycle

$$Cs_2WO_4(cr) + (3Na_2O \cdot 4MoO_3)_{melt}$$
  
= Cs\_2WO<sub>4melt 3Na\_2O \cdot 4MoO\_3</sub>, (3)

$$Cs_2CO_3(cr) + (3Na_2O \cdot 4MoO_3)_{melt}$$
  
= Cs\_2O<sub>melt 3Na\_2O \cdot 4MoO\_3} + CO\_2(g), (4)</sub>

$$WO_{3}(cr) + (3Na_{2}O \cdot 4MoO_{3})_{melt}$$
  
= WO<sub>3melt 3Na<sub>2</sub>O \cdot 4MoO\_{3}. (5)</sub>

The change in enthalpies for reaction (6) at 923 K is

$$Cs_2CO_3(cr) + WO_3(cr) = Cs_2WO_4(cr) + CO_2(g),$$
 (6)

i.e.,  $\Delta H_{923 \text{ K}}^{\circ}$  (6) = -6.6 ± 0.7 kJ/mol.

The reduction of the obtained value to the standard temperature and subsequent calculations are impossible, due to there being no values of the high-temperature enthalpies for  $Cs_2CO_3(cr)$  and  $Cs_2WO_4(cr)$ .

Composition	$\Delta T_{\rm ph.t.},{\rm K}$	<i>T</i> <sub>ph.t.</sub> , K [1]	$\Delta T_{\rm melt},{ m K}$	$\Delta T_{ m solid},{ m K}$	<i>T</i> <sub>melt</sub> , K [1]
Li <sub>2</sub> MoO <sub>4</sub>	_	_	1005-1010	_	975.7 ± 2
$K_2Mo_2O_7$	790–795	—	815-830	810	$765\pm5$
$K_2Mo_3O_{10}$	370-375	—	785-805	780	$845\pm2$
$K_2Mo_4O_{13}$	795-805	—	805-830	810	$834 \pm 2$
$Rb_2Mo_2O_7$	—	—	740-760	730-740	$758\pm5$
$Rb_2Mo_4O_{13triclin}$	—	—	805-825	785-795	$804 \pm 2$
Na <sub>5</sub> La(MoO <sub>4</sub> ) <sub>4tetr</sub>	725-740	—	935-960	950-945	$953 \pm 5$
Li <sub>2</sub> CrO <sub>4hex</sub>	—	$703 \pm 3$	740-765	—	$758 \pm 3$
$Rb_2CrO_4(1)$	1005	$1005 \pm 5$	1180-1205	1215-1205	$1267 \pm 2$
K <sub>2</sub> CrO <sub>4rhombic</sub>	935-945	$939\pm3$	_	—	$1246 \pm 4$
$Rb_5Pr(CrO_4)_4$	—	—	935–945	945-935	—
$Rb_5Sm(CrO_4)_4$	880-890	—	900-920	925-920	—

Table 3. Melting and phase transition temperatures of alkali metal molybdates and chromates

Table 4. Enthalpies of the phase transitions of  $M_2WO_4$  (M = Li, Na, K, Rb, Cs) and melting of  $Na_2WO_{4,cubic}$ 

Composition	$\Delta H_{\mathrm{ph.t}}^{\circ}$ , kJ/mol	Composition	$\Delta H_{\mathrm{ph.t}}^{\circ},\mathrm{kJ/mol}$
Na <sub>2</sub> WO <sub>4, cubic</sub>	3.3 (4.1 ± 0.2 [1])	Rb <sub>2</sub> WO <sub>4, monoclin</sub>	$1.2\pm0.2$
$Na_2WO_{4, cubic}$	34 ± 3.5*	Rb <sub>2</sub> WO <sub>4, rhombic</sub>	$1.0 \pm 0.2$
	(31.5 ± 1.3 [1])	-	-
K <sub>2</sub> WO <sub>4, monoclin</sub>	12 (10.5 ± 1.3 [1])	Rb <sub>2</sub> WO <sub>4, hex</sub>	$2.0 \pm 0.4$
$K_2WO_4$ (II)	$1.2~(1.0\pm0.2~[1])$	Cs <sub>2</sub> WO <sub>4, hex</sub>	$5.8 \pm 1.2$

\* Melting,  $T = 969 \pm 2$  K.



**Fig. 2.** Correlation of enthalpies of formation from oxides of sulfates, selenates, chromates, tungstates, and uranates with those for molybdates.

Using the relative calculation means in [6], we determined the linear correlation between the enthalpies of formation from oxides for sulfates, selenates, chromates, tungstates, and uranates of alkali metals and silver, with analogous values for molybdates (Fig. 2). The standard enthalpies of formation for plotting the correlations were taken from [1].

The linear correlation was established in [7] by comparing the enthalpies of formation of alkali metal isopolymolybdates from oxides according to, e.g., the reaction

$$Na_2O + MoO_3 = Na_2MoO_4$$
(7)

with a change in molar volume for the same reaction in coordinates

$$\Delta H_{\rm ox}^{-1} = (\Delta MV)^{-1}.$$

All lines cross in the same point, forming a bunch of lines. It follows from the familiar equation  $\Delta G_{ox}^{\circ} = \Delta H_{ox}^{\circ} - T\Delta S_{ox}^{\circ}$  that the linear correlation between the Gibbs energy and the change of the molar volume is also valid in coordinates  $(\Delta G_{ox}^{\circ})^{-1} - ((\Delta MV)_{ox})^{-1}$ . Such



Fig. 3. Correlation of Gibbs energies of formation and the density of isopolymolybdates in coordinates  $(\Delta G_{\text{ox}}^{\circ})^{-1} - ((\Delta M V_{\text{ox}})^{-1})^{-1}$ .

a correlation for the family of alkali metal isopolymolybdates is shown in Fig. 3.

#### CONCLUSIONS

Based on the density values of molybdate [2] and the corresponding oxides, we can determine the unknown thermodynamic characteristics of a sought compound.

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